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ABSTRACT: Gas chromatography/mass spectrometry was used to analyze the pyrolytic byproducts from an Army-unique propellant compound (AA2) that is composed of predominantly nitrocellulose and nitroglycerin. Compounds produced by AA2 pyrolysis were compared to compounds detected in the gaseous effluent from AA2 incineration. The light permanent gases and most of the higher molecular weight byproducts produced by AA2 incineration are replicated by laboratory pyrolysis on AA2. The reverse case also holds whereby 18 out of 24 high molecular weight AA2 pyrolytic byproducts are found in the incinerator emissions. Poor matching, however, was obtained between the two processes for the volatile, water-soluble species. None of these low molecular weight compounds produced under pyrolytic conditions were detected in the AA2 incinerator samples, likely indicating inefficient capture of these compounds from the effluent stream. Separate pyrolytic degradation of the individual components of AA2 provides evidence that nearly all of the incomplete combustion products detected during incineration originate not from the prevalent energetic ingredients but rather from the minor and trace additives in AA2. In addition, pyrolysis successfully identified the AA2 components capable of surviving the incineration process intact. This work illustrates the potential of bench-scale pyrolysis for predicting incineration behavior.

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Preface

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Gas chromatography/mass spectrometry was used to analyze the pyrolytic byproducts from an Army-unique propellant compound (AA2) that is composed of predominantly nitrocellulose and nitroglycerin. Compounds produced by AA2 pyrolysis were compared to compounds detected in the gaseous effluent from AA2 incineration. The light permanent gases and most of the higher molecular weight byproducts produced by AA2 incineration are replicated by laboratory pyrolysis on AA2. The reverse case also holds whereby 18 out of 24 high molecular weight AA2 pyrolytic byproducts are found in the incinerator emissions. Poor matching, however, was obtained between the two processes for the volatile, water-soluble species. None of these low molecular weight compounds produced under pyrolytic conditions were detected in the AA2 incinerator samples, likely indicating inefficient capture of these compounds from the effluent stream. Separate pyrolytic degradation of the individual components of AA2 provides evidence that nearly all of the incomplete combustion products detected during incineration originate not from the prevalent energetic ingredients but rather from the minor and trace additives in AA2. In addition, pyrolysis successfully identified the AA2 components capable of surviving the incineration process intact. This work illustrates the potential of bench-scale pyrolysis for predicting incineration behavior.

Introduction

Munitions production by the armaments industry annually generates approximately 1600 t of hazardous waste containing explosives and propellants (1). Several military installations have opted to use hazardous waste incinerators to dispose of much of this energetic material (2). Although incineration is a mature technology for the thermal destruction of energetic materials and waste, fear of hazardous input feed constituents and products of incomplete combustion (PIC) potentially emitted by the incinerator limits public acceptance. Byproducts generated by incineration are a function of the chemical components of the waste feed; the

molecular composition of the energetic compounds in the waste; and the operating conditions such as waste feed rate, temperature, and residence time (2). A bench-scale method capable of predicting incineration performance could test and optimize operational parameters off-line, identify the level of effluent control required to capture and eliminate recalcitrant components, and assess the potential of incineration for new waste streams.

Numerous studies on high-temperature degradation of organic compounds have recognized that, as compared to oxygen-rich atmospheres or stoichiometric ratios of required oxygen to waste, oxygen-deficient conditions produce the most complex mixtures of PIC at the highest concentrations (3–7). Most bench-scale laboratory experiments have studied waste containing chlorinated compounds (3–14) because of the potential creation of products far more toxic and persistent than the input feed constituents. Results from these experiments illustrate that, when compared to oxygen-rich conditions, PIC generated under oxygen-deficient conditions are more numerous, the molecular weight and the distribution increases, and the maximum yields and temperature stability of the byproducts increase. Work by Dellinger and co-workers on thermal degradation of municipal-type waste in atmospheres of varying oxygen content shows that byproducts generated under very low or no oxygen content conditions best match the PIC generated during incineration of these same wastes (15–18). It is postulated that, under conditions of excess oxygen, all input constituents are completely oxidized to innocuous light permanent gases. In areas of low oxygen content known as “pyrolytic pockets” (17), PIC are created. These areas are associated with poor micromixing of oxygen, fuel, and waste (5, 6, 11, 18–20). Replication of these pyrolytic pockets in the laboratory would generate the same PIC as incineration of the waste under worst-case conditions (12). It has also been shown that destruction and removal efficiencies of recalcitrant organic compounds in oxygen-deficient environments correlate well with full-scale emission data (3). Several researchers have concluded that laboratory pyrolysis can provide valuable qualitative modeling of the incineration of municipal waste (7, 16–18). Accurate quantitative prediction of incineration emissions is unlikely, however, because of temporal fluctuations in operating conditions and the complex dynamic microenvironments present during incineration (16).

Pyrolysis combined with gas chromatography/mass spectrometry (GC/MS) is an analytical technique used to study materials that are not amenable to direct injection into the GC/MS such as polymers, paints, oils, microorganisms, and soil (21). This research studies the ability of the pyrolysis chamber to simulate the PIC evolving from an incinerator. The GC/MS serves as a monitoring instrument to collect and characterize the thermal degradation products from pyrolysis. Data were collected from the pyrolysis of a munitions propellant (AA2) as well as pyrolysis on each separate AA2 constituent. AA2 was also incinerated at a military installation, and the emissions from the rotary kiln were analyzed. This research qualitatively compares the emission data from full-scale incineration of AA2 to the pyrolytic degradation products of AA2.

Experimental Methods

Incineration. The incinerator system consists of a rotary kiln 12 ft long and 5.5 ft in diameter followed by pollution control equipment such as a secondary combustion chamber, an evaporative cooler, and a baghouse for dust collection. An aqueous slurry of the AA2 waste stream, containing ap-

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proximately 15% solids, is metered into the rotary kiln at a feed rate of approximately 280 lb of slurry/h. The kiln operates at approximately 550–750 °C, causing the water to evaporate and the energetic materials to combust. The sampling location for the collection probes was immediately downstream from the rotary kiln. Sampling at this point ensured that any collected byproducts result from the initial incineration process alone, without additional treatment and scrubbing from the pollution control devices present further downstream.

Sampling and Analysis for the Incineration Process. Four separate sampling trains were used for emissions collection including one for hydrogen cyanide (HCN), one for volatile organic compounds (VOC), one for semivolatile organic compounds (SVOC), and one for permanent gases. HCN was collected and analyzed using NIOSH Method 7904 (22). The continuous emissions monitor (CEM) analyses were completed in accordance with EPA Methods 3A (O₂ and CO₂), 7E (NO_x), 10 (CO), and 25A (total hydrocarbons) (23–26). Data were collected from the CEM over the entire AA2 incineration burn. Equipment problems precluded the use of data from the total hydrocarbon CEM.

A volatile organic sampling train and collection method as described in EPA Method 0030 (27) was used to collect VOC. This train is a Tenax cartridge, an impinger for collection of liquid condensate, and a Tenax/activated charcoal cartridge connected in series. Sampling from the rotary kiln port used a flow rate of 1 L/min for 20 min. The Modified Method 5 sampling train includes a particulate filter, an XAD resin-filled trap, and an impinger for condensate to collect SVOC following EPA Method 0010 (28). The SVOC sampling time was 5 h, performed anisokinetically on the basis of estimations of the gas velocity at the kiln port location.

All VOC and SVOC samples were extracted using EPA Method 5041A (29) and EPA Method 0010 (28), respectively, and then analyzed using a Saturn I GC/MS (Varian, Walnut Creek, CA). For VOC analysis, a DB624 column (J & W Scientific, Folsom, CA), 30 m × 0.25 mm × 1.4 μm film thickness, was used. The mass scan for the ion trap used a mass range of 60–260 amu. Although this choice of the lower mass value eliminated many background interferences, it also eliminated important daughter peaks from the mass spectra, frequently making identification difficult. For SVOC analysis, a DB17MS column (J & W Scientific), 30 m × 0.25 mm × 0.25 μm film thickness, was used. The mass scan for SVOC analyses used a mass range of 50–430 amu. Further details on the sampling and analysis of the incinerator effluent stream are available elsewhere (30).

Laboratory Pyrolysis. The instrumentation for laboratory pyrolysis consisted of a Pyroprobe 2000 (CDS, Oxford, PA) interfaced directly onto an HP 5890 GC/5970 MS (Agilent Technologies, Palo Alto, CA). Two different pyrolytic experiments were performed on each sample to investigate the entire range of potential byproducts. In configuration A, a PoraPLOT Q column (ChromPack, Raritan, NJ), 50 m × 0.32 mm i.d. × 10 μm film thickness, was used for separation of the low molecular weight (MW) species. The GC oven program began at 40 °C for 2 min, ramped to 200 °C at 10 °C/min, and stayed at 200 °C for 2 min. Configuration B used an Agilent Technologies HP5MS column, 25 m × 0.20 mm i.d. × 0.33 μm film thickness, for separation of higher MW species. The GC oven program began at 40 °C for 2 min, ramped to 250 °C at 10 °C/min, and stayed at 250 °C for 7 min. Both configurations employed a splitless injection mode.

Preparation of the samples and the pyrolysis temperature profile have been described in detail elsewhere (31). Approximately 2 mg of a sample was loaded into a quartz tube. This prepared tube was placed inside a platinum wire coil on the probe, which was inserted into the pyrolysis chamber. The pyrolysis temperature program heated the sample from

100 to 900 °C at a rate of 20 °C/ms and held it at 900 °C for 100 s. The pyrolysis chamber was maintained at 150 °C. The helium carrier gas swept the pyrolysate from the chamber onto the GC column at a flow rate of 1 mL/min.

Samples. Propellants that contain two explosive ingredients are termed double-base propellants (32). The double-base propellant AA2 is composed of the following ingredients in order of decreasing percentage: nitrocellulose (NC) (approximately 50% of AA2 by weight), nitroglycerin (NG) (40%), triacetin (3%), di-*n*-propyladipate (2%), 2-nitrodiphenylamine (NDPA) (2%), and candelilla wax (0.1%). Samples of AA2 were obtained directly from the input waste stream to the incinerator. Samples of explosive grade 13.4%-nitrated NC (Picatinny Arsenal, NJ), 1.0 mg/mL NG in acetonitrile (Radian Corporation, Austin, TX), triacetin (J. T. Baker, Phillipsburg, NJ), di-*n*-propyladipate (Fisher, Pittsburgh, PA), and NDPA and candelilla wax (Aldrich, Milwaukee, WI) were also obtained for individual pyrolytic investigation and were used as received.

Results

AA2 Incineration Background Samples. The incinerator operated without an input waste feed for several hours prior to AA2 incineration to provide background samples for VOC, SVOC, HCN, and CEM analyses. In the background VOC and SVOC samples (30), toluene was the major component followed by benzene, xylene, and other alkylbenzenes. It has been noted that toluene and benzene as well as other larger polycyclic aromatic compounds can result from combustion of natural gas in a fuel-rich flame (33). Past history of this incinerator includes the burning of dinitrotoluene (DNT), which could also be a source of aromatics from deposition of byproducts on interior surfaces of the kiln.

HCN was not detected in the background samples. The concentration levels for the light gases measured by CEM over the background period proved to be relatively constant at 13.5% O₂, 3.8% CO₂, 50 ppm NO_x, and 10 ppm CO.

VOC from the Incineration of AA2. Analysis of the AA2 VOC adsorbent trap detected primarily the background peaks benzene, toluene, and xylene but also observed VOC PIC generated by AA2 incineration including benzofuran, benzonitrile, and naphthalene (30). Several byproducts defy identification because of a saturated mass spectrum. Analysis of the VOC impinger detected the presence of the polar byproducts 2,5-dihydro-1H-pyrrole, dimethylcyanamide, 2(5H)-furanone, 2-furancarboxaldehyde, benzaldehyde, 2-hydroxybenzaldehyde, and 2-nitrophenol (30). VOC samples were collected in duplicate, and both contained identical byproducts.

SVOC from the Incineration of AA2. Analysis of the SVOC from incineration of AA2 proved to be richer in information than VOC analysis. Successful identification of many of the smaller peaks was achieved by a subsequent analysis of the same sample using a quadrupole GC/MS with a lower detection mass value of 10 amu (30). Table 1 lists the compounds found in the extraction of the XAD resin. Four undergraded AA2 components were detected: NG, triacetin, di-*n*-propyladipate, and NDPA. All PIC detected are aromatic species. Analysis of the extract of the particulate filter and the condensate water uncovered no additional byproducts (30). SVOC samples were also collected in duplicate and contained the same products.

HCN and CEM Measurements during Incineration of AA2. HCN was not found in any of the samples collected during AA2 incineration. Unfortunately, the 5-day holding time was exceeded before analysis, and several samples were found to be more acidic than recommended (pH > 13).

The CEM data provide only broad conclusions. During incineration of AA2, the levels of CO₂, NO_x, and CO increase in abundance to 5.5%, 650 ppm, and 200 ppm, respectively,

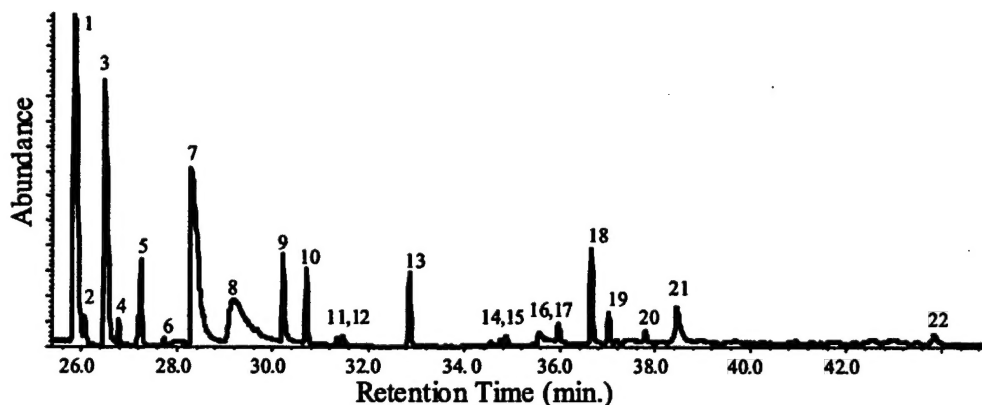


FIGURE 1. Pyrogram of low MW byproducts from pyrolysis of AA2 using configuration A.

TABLE 1. SVOC Detected during Incineration of AA2

| | |
|----------------------|--|
| toluene | hexanedioic acid, bis(1-methyl ethyl) ester |
| naphthalene | 4-hydroxy-4-methyl-2-pentanone |
| phenol | quinoxaline |
| benzaldehyde | isoquinoline |
| benzofuran | ethylbenzoic acid |
| benzonitrile | triacetin |
| benzoxazole | di- <i>n</i> -propyladipate |
| benzoquinone | phenazine |
| hydroxybenzaldehyde | carbazole |
| nitrobenzene | bis(<i>p</i> - <i>tert</i> -butylphenyl)ether |
| pyridinecarbonitrile | NDPA |
| 2-nitrophenol | 2-nitro- <i>N</i> -(4-nitrophenyl)benzamine |
| 3-phenyl-2-propanol | NG |

TABLE 2. Identification of Low MW Pyrolytic Byproducts from AA2 As Shown in Figure 1

| peak | identification | peak | identification |
|------|------------------------|------|-----------------------------|
| 1 | CO, NO, N ₂ | 12 | methanol |
| 2 | methane | 13 | ethylene oxide/acetaldehyde |
| 3 | CO ₂ | 14 | 1-buten-3-yne |
| 4 | N ₂ O | 15 | butadiene |
| 5 | ethene | 16 | formic acid |
| 6 | ethane | 17 | acetonitrile |
| 7 | water | 18 | 2-propenal |
| 8 | formaldehyde | 19 | furan |
| 9 | HCN | 20 | 2-propenenitrile |
| 10 | propene | 21 | acetic acid |
| 11 | propyne | 22 | methyl formate |

indicating that these light gases are incineration byproducts. Similarly, O₂ levels decrease from background levels to 11% since oxygen is consumed during combustion.

AA2 Pyrolysis—Low MW Byproducts. Since incineration is performed on a slurried mixture of AA2 and water, pyrolysis was initially performed on a slurried sample taken from the incinerator input feed. A sample of this slurry was also dried at room temperature and was pyrolyzed. Except for relative changes in abundances, there were no qualitative differences in the byproducts present in these two pyrolysates. The ease of sample manipulation led to the use of dried AA2 for these pyrolytic studies.

Figure 1 is a pyrogram of the light MW byproducts from pyrolysis of AA2 using configuration A. Table 2 lists the peak identifications of these byproducts from mass spectral matching. Excellent matches were obtained for all peaks. Peak 1 is an unresolved combination of light permanent gases such as CO, NO, and N₂. Peak 13 is identified as either ethylene oxide or acetaldehyde, which have nearly identical mass spectra. Pyrolysis of AA2 using temperatures from 300 to 900 °C produced pyrograms similar to Figure 1. In addition,

altering the pyrolysis times from 10 to 100 s or utilizing sample masses from 0.5 to 2.4 mg had little effect on the pyrogram features; 900 °C and 100 s were chosen as the pyrolysis temperature and time to maximize byproduct abundance while minimizing carryover contamination between runs.

AA2 Pyrolysis—High MW Byproducts. Figure 2 is a pyrogram of the higher MW pyrolytic byproducts separated and analyzed using configuration B. Table 3 lists the peak identifications for this pyrogram. The abundance of these heavier pyrolytic byproducts is generally less than the abundance of the light MW pyrolytic byproducts seen in Figure 1. The compounds that are well-separated using configuration A elute as unresolved peaks 1 and 2 and contribute nearly 90% of the total peak area.

Four initial components of AA2 are noted in Table 3 as compounds capable of vaporizing before thermally degrading: triacetin (peak 18), NG (peak 19), di-*n*-propyladipate (peak 21), and NDPA (peak 24). All remaining peaks are produced via pyrolytic mechanisms from AA2 components. Most are aromatic compounds, and all have some form of unsaturation.

Pyrolysis of Individual Components of AA2. Pyrolysis was performed on six different components of AA2 to determine the separate contributions of each. Since nearly none of the pyrolytic byproducts of AA2 using configuration A were observed in the incinerator VOC samples, configuration B pyrolysis on the individual components of AA2 is the primary focus. Pyrolysis of the separate components using configurations A and B are presented elsewhere (31), and only the major peaks are discussed below.

NC and NG Pyrolysis. NC is an energetic macromolecule with multiple C-O-NO₂ groups, classifying it as a nitrate ester. Substantial thermal breakdown into light gases is expected. Pyrolysis of NC using configuration A results in a pyrogram that is nearly identical to the pyrogram of AA2 shown in Figure 1, including production of furan (31). A pyrogram performed on NC using configuration B shows few identifiable peaks (31). The lighter MW gases coelute as a large peak that interferes with the mass spectral data of the smaller peaks atop it. Excellent spectral matching and identification occur only for 2-furancarboxaldehyde, 2(5H)-furanone, and 2H-pyran-2-one.

NG is a highly energetic nitrate ester containing three C-O-NO₂ groups per molecule. Similar to NC, pyrolysis using configuration A produces the bulk of the pyrolytic byproducts including formaldehyde, ethylene oxide, ethyl acetate, and ethylenediamine. The configuration B pyrogram is dominated by the light MW product peak, but a small NG peak is also observed indicating that NG is volatile enough to escape the pyrolysis chamber before degradation (31).

Triacetin Pyrolysis. A pyrogram of triacetin using configuration B has three main features (31). Acetic acid is the

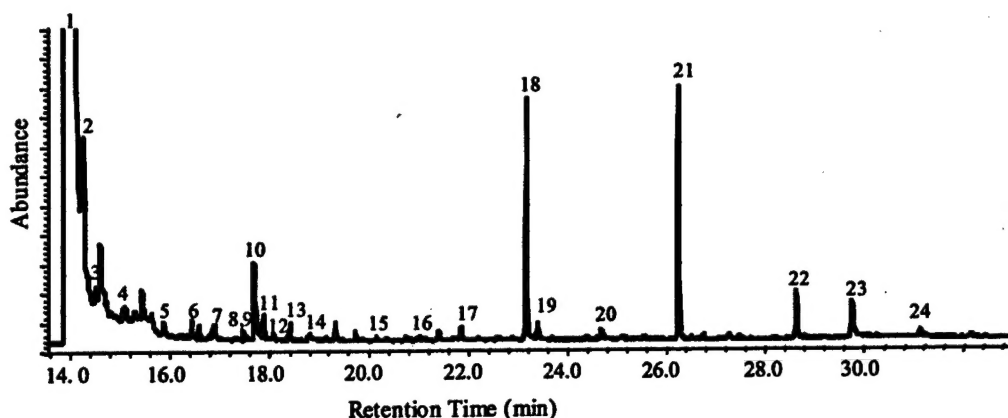


FIGURE 2. Pyrogram of high MW byproducts from pyrolysis of AA2 using configuration B.

TABLE 3. Identification of the High MW Pyrolytic Byproducts from AA2 As Shown in Figure 2

| peak | identification | peak | identification |
|------|----------------------------|------|---------------------|
| 1 | low molecular weight gases | 13 | benzoxazole |
| 2 | acetic acid | 14 | hydroxybenzaldehyde |
| 3 | 2-butenal | 15 | 2-nitrophenol |
| 4 | pyridine | 16 | naphthalene |
| 5 | 2-furancarboxaldehyde | 17 | isoquinoline |
| 6 | styrene | 18 | triacetin |
| 7 | p-benzoquinone | 19 | NG |
| 8 | isocyanatobenzene | 20 | 2-ethenylquinoline |
| 9 | benzaldehyde | 21 | di-n-propyladipate |
| 10 | phenol | 22 | phenazine |
| 11 | benzonitrile | 23 | carbazole |
| 12 | benzofuran | 24 | NDPA |

major pyrolytic byproduct, a result of elimination from the three ends of the triacetin molecule. A narrow peak consisting of the unresolved light permanent gases is present. Finally, a large triacetin peak is observed, indicating that it can quickly vaporize upon rapid heating.

Di-n-propyladipate Pyrolysis. Due to similar structures, di-n-propyladipate and triacetin have several common features in their pyrograms (31). Prominent peaks for light gases and acetic acid are present as well as smaller peaks of benzene, toluene, styrene, indene, and naphthalene. Non-aromatic pyrolytic byproducts are the five-membered ring structures cyclopentanone and cyclopentenone. The major feature in this pyrogram is the large, broad, tailing peak due to the di-n-propyladipate that is not thermally decomposed.

Candelilla Wax Pyrolysis. Candelilla wax is a complex mixture of long-chain hydrocarbons and long hydrocarbon chain alcohols and esters. Pyrolysis of this wax gives a rich characteristic pyrogram arising from the random scission of the hydrocarbon chains (31). After the light gas peak, a series of triplets is observed as expected (21). Each triplet is the diene, alkene, and alkane for hydrocarbon chains of carbon length 10–30, with the center alkene peak dominating.

NDPA Pyrolysis. The pyrogram of NDPA using configuration B is shown in Figure 3 with its structure in the inset. Table 4 identifies the peaks numbered in Figure 3. NDPA pyrolyzes into a large number of products that originate from its diphenylamine structure, but the broad peak of NDPA indicates that much of this compound also vaporizes onto the analytical column.

Discussion

Table 5 is a compilation of all incinerator emission products from both VOC and SVOC samples. The first column is the compound name, the second column identifies the incin-

erator sample containing this compound, and the last column is the AA2 constituent that also produces this compound when pyrolyzed. The origin of most of the incinerator emissions can be deduced from these data.

Ten PIC are not generated by pyrolysis and therefore may be the result of secondary heterogeneous combustion interactions in the incinerator. Dimethylcyanamide, pyridinecarbonitrile, and 2,5-dihydro-1H-pyrrole are derived from nitrogen-containing components of AA2 but are not observed in any pyrolysis experiments on AA2, NC, NG, or NDPA. 2-Nitro-N-(4-nitrophenyl)benzamine is also not observed during AA2 pyrolysis. Because of very similar structures, it likely originates from reactions involving NDPA, although it is not observed during NDPA pyrolysis. These four compounds together with phenylpropenol, ethylbenzoic acid, bis(p-tert-butylphenyl) ether, and the hexanedioic acid ester are exceedingly minute. Methylnitrophenol is probably derived from NDPA reactions since only this compound generates nitrophenol during pyrolysis. 4-Hydroxy-4-methyl-2-pentanone is the major incineration byproduct from AA2 that is not generated by pyrolysis. This compound is also detected in the SVOC samples from the incineration of other waste streams that contain NC and NG (30).

Xylene and nitrobenzene are examples of PIC that are not seen in the pyrogram of AA2 yet are observed during the pyrolysis of one of its minor constituents (candelilla wax and NDPA, respectively). The small amount of these additives present in a 2-mg sample of AA2 minimizes many of the pyrolytic byproducts originating from these compounds. Appreciable amounts of these byproducts, however, can collect in the incineration samples since the cumulative mass of an additive incinerated over a 1–5-h collection time becomes substantial.

Benzaldehyde, hydroxybenzaldehyde, and benzoquinone are incineration byproducts that are also produced by pyrolysis of AA2 but are not produced pyrolytically by any individual component of AA2. This indicates some secondary interactions among AA2 components or byproducts under high-temperature pyrolytic conditions, but the small relative abundances of these byproducts prove these interactions to be minimal.

On the basis of the relative abundance of the peaks, the low MW pyrolysis byproducts are predicted to be the major incineration PIC from AA2. Only the light permanent gases from these samples, however, are detected in the incinerator samples. These collection techniques are not optimized for the collection of volatile, water-soluble species. Pyrolysis experiments prior to incinerator emission sampling would permit optimization of the collection trains and analytical methods to collect and analyze for particular compounds. HCN is also predicted to be a substantial byproduct from the pyrolysis data but was not detected in any AA2 incineration

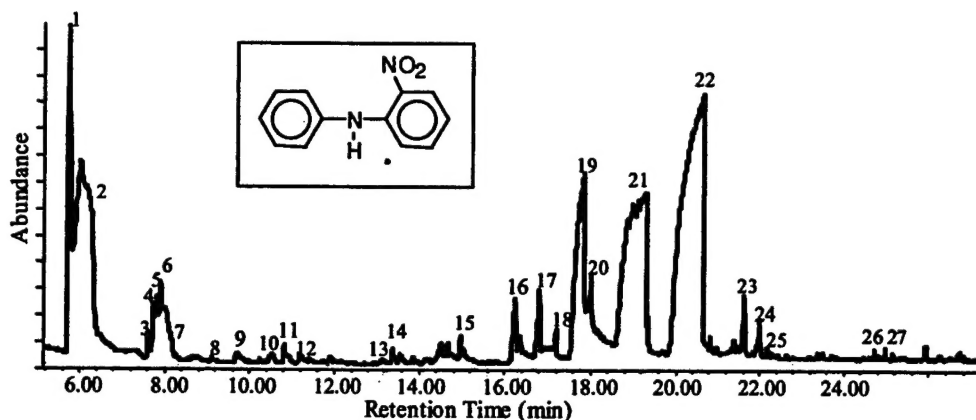


FIGURE 3. Pyrogram of 1.6 mg of NDPA using configuration B. The structure of NDPA is shown in the inset.

TABLE 4. Identification of NDPA Pyrolytic Byproducts from Figure 3

| peak | identification | peak | identification |
|------|------------------------|------|--|
| 1 | light gases | 15 | dibenzofuran |
| 2 | benzene | 16 | diphenylamine |
| 3 | isocyanatobenzene | 17 | 5 <i>H</i> -indeno[1,2- <i>b</i>]pyridine |
| 4 | phenol | 18 | 9 <i>H</i> -pyrido[3,4- <i>b</i>]indole |
| 5 | aniline | 19 | phenazine |
| 6 | benzonitrile | 20 | 4-(phenylamino)phenol |
| 7 | benzoxazole | 21 | carbazole |
| 8 | nitrobenzene | 22 | NDPA |
| 9 | 2-nitrophenol | 23 | phenoxazine |
| 10 | azulene | 24 | 3-nitrocarbazole |
| 11 | quinoxaline | 25 | 4-dibenzofuranamine |
| 12 | isoquinoline | 26 | 2,2'-biquinoline |
| 13 | biphenyl | 27 | 9-phenyl-9 <i>H</i> -carbazole |
| 14 | <i>o</i> -nitroaniline | | |

sample due to problems noted earlier. In contrast, most of the higher MW pyrolysis products in Table 3 are present in the incineration samples.

Although NC is a major component of AA2, the configuration B pyrolysis data predict that it contributes very little to the incineration byproducts collected by the SVOC train and is not an emission concern because of its large molecular weight. It can, however, produce toxic furan products. NG is the other major component of AA2, yet it contributes even fewer high MW byproducts. The presence of NG in the pyrogram correctly predicts the presence of NG in incineration emissions. The ability of NG to vaporize and escape rather than degrade pinpoints the need to monitor NG degradation during secondary effluent treatment (which this facility does). Pyrolysis also correctly predicts that triacetin, di-*n*-propyladipate, and NDPA will be detected in the effluent stream. NDPA pyrolytic byproducts contribute a majority of the observed incinerator SVOC emissions. The distinctive hydrocarbon series from the pyrolysis of candelilla wax is not observed in any of the incinerator samples, which is not surprising since candelilla wax is present in AA2 at less than 0.1%. Pyrolysis experiments can predict the components of a waste that may survive the incineration process, determine the PIC that can evolve from each component separately or in combination with other species, and pinpoint the components that contribute the most troublesome emissions. In this case, although NC and NG compose 90% of AA2, the behavior of the minor additives of AA2 dominates the SVOC fraction of the incinerator byproducts, and one compound (NDPA) was the primary source of most of the unwanted byproducts. Future work will expand on collection and analytical methods to provide comparative quantitative examination of emission data from these thermal processes.

TABLE 5. List of Incinerator Byproducts and the AA2 Component That Generates This Byproduct Pyrolytically^a

| compound | incinerator sample | AA2 component |
|---|--------------------|------------------|
| benzene | VT | 1, 2, 3, 4, 5, 6 |
| toluene | VT, VW | 1, 2, 3, 4, 6 |
| benzofuran | VT, ST | A, 4 |
| benzonitrile | VT, ST | A, 5 |
| naphthalene | VT, ST | A, 4, 6 |
| dimethylcyanamide | VW | |
| 2-furancarboxaldehyde | VW | A, 1 |
| benzaldehyde | VW, ST | A |
| hydroxybenzaldehyde | VW, ST | A |
| 2-nitrophenol | VW, ST | A, 5 |
| xylene | VT | 6 |
| phenol | ST | A, 5 |
| benzoxazole | ST | A, 5 |
| nitrobenzene | ST | 5 |
| 4-hydroxy-4-methyl-2-pentanone | ST | |
| benzoquinone | ST | A |
| pyridinecarbonitrile | ST | |
| isoquinoline | ST | A, 5 |
| ethylbenzoic acid | ST | |
| triacetin | ST | A, 3 |
| di- <i>n</i> -propyladipate | ST | A, 4 |
| phenazine | ST | A, 5 |
| carbazole | ST | A, 5 |
| bis(<i>p</i> - <i>tert</i> -butylphenyl) ether | ST | |
| NDPA | ST | A, 5 |
| 2-nitro- <i>N</i> -(4-nitrophenyl)benzamine | ST | |
| 3-phenyl-2-propanol | ST | |
| hexanedioic acid, bis(1-methylethyl) ester | ST | |
| 2,5-dihydro-1 <i>H</i> -pyrrole | VW | |
| 2(5 <i>H</i>)-furanone | VW | 1 |
| methylnitrophenol | VW | |
| NG | ST | A, 2 |

^a The incinerator sample column indicates where the sample was detected according to the following notation: VT = VOC trap, VW = VOC impinger, and ST = SVOC trap. The third column denotes the starting material that also generated the same byproduct when pyrolyzed using the following legend: A = AA2, 1 = NC, 2 = NG, 3 = triacetin, 4 = di-*n*-propyladipate, 5 = NDPA, and 6 = candelilla wax.

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Literature Cited

- (1) J. M. Stratta and Associates, Inc.; Life Systems, Inc. *Open Burning-Open Detonation Waste Generation Survey and Al-*

- ternatives Research Study*; Report for the U.S. Army Construction Engineering Research Laboratory (CERL), August 1993.
- (2) Subsinsky, M. A.; Life Systems, Inc. *Identification and Quantification of Energetic Waste Incinerators and Air Emissions from Energetic Waste Incineration*; Report for CERL, November 1993.
 - (3) Taylor, P. H.; Dellinger, B. *Environ. Sci. Technol.* **1988**, *22*, 438.
 - (4) Young, C. M.; Voorhees, K. J. *Chemosphere* **1992**, *24*, 525.
 - (5) Taylor, P. H.; Dellinger, B.; Tirey, D. A. *Int. J. Chem. Kinet.* **1991**, *23*, 1051.
 - (6) Fisher, E. M.; Koshland, C. P. *Combust. Flame* **1992**, *90*, 185.
 - (7) Graham, J. L.; Hall, D. L.; Dellinger, B. *Environ. Sci. Technol.* **1986**, *20*, 703.
 - (8) Young, C. M.; Voorhees, K. J. *Chemosphere* **1991**, *23*, 1265.
 - (9) Taylor, P. H.; Tirey, D. A.; Rubey, W. A.; Dellinger, B. *Combust. Sci. Technol.* **1994**, *101*, 75.
 - (10) Lee, W.-J.; Cicek, B.; Senkan, S. M. *Environ. Sci. Technol.* **1993**, *27*, 949.
 - (11) Vitovec, W.; Koshland, C. P.; Lucas, D.; Sawyer, R. F. *Combust. Sci. Technol.* **1996**, *116-117*, 153.
 - (12) Tirey, D. A.; Taylor, P. H.; Kasner, J.; Dellinger, B. *Combust. Sci. Technol.* **1990**, *74*, 137.
 - (13) Young, C. M.; Voorhees, K. J. *Chemosphere* **1992**, *24*, 681.
 - (14) Duvall, D. S.; Rubey, W. A.; Mescher, J. A. EPA Project Summary, EPA/600/9-80/011. *Treatment of Hazardous Waste. Proceedings of the Sixth Annual Research Symposium*, Chicago, IL, March 1980.
 - (15) Dellinger, B.; Taylor, P. H.; Tirey, D. A. EPA Project Summary, EPA/600/S2-90/039. *Minimization and Control of Hazardous Combustion Byproducts*, May 1991.
 - (16) Dellinger, B.; Hall, D. L.; Graham, J. L.; Mazer, S. L.; Rubey, W. A.; Malanchuk, M. EPA Project Summary, EPA/600/S2-86/006. *PIC Formation under Pyrolytic and Starved Air Conditions*, July 1986.
 - (17) Tirey, D. A.; Striebich, R. C.; Dellinger, B.; Bostian, H. E. *Hazard. Waste Hazard. Mater.* **1991**, *8*, 201.
 - (18) Taylor, P. H.; Dellinger, B.; Lee, C. C. *Environ. Sci. Technol.* **1990**, *24*, 316.
 - (19) Sidhu, S.; Kasti, N.; Edwards, P.; Dellinger, B. *Chemosphere* **2001**, *42*, 499.
 - (20) Tanada, T. N.; Velazquez, J.; Hemmi, N.; Cool, T. A. *Combust. Sci. Technol.* **1994**, *101*, 333.
 - (21) Wampler, T. *Applied Pyrolysis Handbook*; Marcel Dekker: New York, 1995.
 - (22) U.S. Department of Health, Education, and Welfare. *NIOSH Manual of Analytical Methods, Method 7904, Cyanides, aerosol and gas*; August 15, 1994.
 - (23) U.S. Environmental Protection Agency. *Code of Federal Regulations*, Section 40, Part 60, Method 3A, 1996; p 604.
 - (24) U.S. EPA. *Code of Federal Regulations*, Section 40, Part 60, Method 7E, 1996; p 725.
 - (25) U.S. EPA. *Code of Federal Regulations*, Section 40, Part 60, Method 10, 1996; p 758.
 - (26) U.S. EPA. *Code of Federal Regulations*, Section 40, Part 60, Method 25A, 1996; p 949.
 - (27) U.S. EPA, Office of Solid Waste and Emergency Response. *SW-846, Method 0030*; September 1986.
 - (28) U.S. EPA, Office of Solid Waste and Emergency Response. *SW-846, Method 0010*, September 1986.
 - (29) U.S. EPA, Office of Solid Waste and Emergency Response. *SW-846, Method 5041A*, January 1995.
 - (30) Cropek, D.; Day, J.; Kemme, P. *Incineration By-Products of AA2, NC Fines, and NG Slums*; ERDC/CERL TR-01-64; September 2001; http://owwww.cecer.army.mil/techreports/cropek_incineration/cropek_incineration.pdf.
 - (31) Cropek, D.; Kemme, P.; Day, J. *Pyrolytic Decomposition Studies of AA2, A Double-Base Propellant*; ERDC/CERL TR-01-66; October 2001; http://owwww.cecer.army.mil/techreports/Cropek_Pyrolysis_Decomposition/Cropek_Pyrolysis_decomposition.pdf.
 - (32) Urbanski, T. *Chemistry and Technology of Explosives*; Pergamon Press: New York, 1964; Vol. 3.
 - (33) Toqan, M.; Thijssen, J.; Beer, J. M.; Lafleur, A. J. *Inst. Energy* **1993**, *66*, 119-125.

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